REMARKS

Claims 2, 4, 6, 8, 9, and 12-28 are presented for consideration by the Examiner. Claim 1 has been cancelled in favor of relying on claims 6 and 8 to cover the single layer and multi-layer embodiments. TFE/PMVE/PPVE (MFA) copolymer has been deleted from claims 6 and 20 in favor of new claims 24 and 25 being directed to the MFA copolymer. As disclosed on p. 11, l. 36-38, the MFA copolymer can be stabilized or unstabilized. Thus, the stabilization required for the copolymer in claims 6 and 20 is not required for the MFA copolymer of claims 24 and 25.

Claim 6 has been amended to recite as follows:

(a) that the stabilized copolymer and metal powder are the essential ingredients in the composition to accomplish both bubble free and adhesion results,
(b) the minimum adhesion (peel strength) of the rotolining (p. 11-14),
(c) that stabilization of the copolymer is by fluorine treatment (p. 3, l. 17) to distinguish from Buckmaster who dislikes fluorine treatment (col. 2, l. 3-12)
(d) to incorporate the subject matter of claim 7, now cancelled.

The consisting essentially subject matter, fluorine treatment and maximum metal powder content have been incorporated into claim 20 and new claims 24 and 25, and the minimum adhesion has been incorporated into claim 25. Claim 20 has been additionally amended to recite that the powder is metal to be consistent with claim 6.

Claim 8 has been amended to delete the reference to overcoat thickness consistent with the role of the overcoat (p. 10, l. 14). Claims 2 and 4 reciting overcoat thickness have been amended to depend on claim 8. New claims 22 and 26 recite the preferred metal powder content (p. 12, l. 14-15). New claims 23 and 27 recite the form of the composition, namely that it is a mixture of the copolymer particles and the metal powder (p. 11, l. 36-37), so as to distinguish from Saito et al. (Saito) who discloses the necessity of incorporating the adhesion-promoting ingredients into the PFA granules (paragraph bridging cols. 4 and 5). Thus, new claims 23 and 27 cover the simple mixture of copolymer particles and metal powder, not the copolymer particles containing the metal powder. New claim 28 recites a minimum overcoat thickness of at least 4 mm (p. 10, l. 35-37).

With respect to the double patenting rejection of claims 6 and 17 over certain claims of U.S. Patent 6,632,902, reconsideration is respectfully requested on the basis that claim 6 is not substantially identical to the '902 claims. The '902 claims merely recite the stabilized TFE copolymer particles, but not the presence of the small amount of metal powder and the adhesion result as recited in claim 6 of the present application. Another difference arises from the Claim 2 ('902) recitation of rotomolding, which as explained in Example 4 of '902 involves removal of the molded article from the mold. This is possible because the stabilized

tetrafluoroethylene/perfluoro(alkyl vinyl ether) (TFE/PAVE) copolymer does not adhere to the mold. In contrast, claim 6 of the present application is a rotolining process wherein the presence of the metal powder enables the rotolining to adhere to the mold surface. The rotolining process of claim 6 (and 17) is not patentably indistinct from the rotomolding process claims of '902.

With respect to the 112 rejection, the amendment to claim 6, adding "metal" to the description of the powder addresses this rejection.

With respect to the novelty rejection now applicable to claims 6, 12, 14, and 19-21 based on Kazumi's disclosure of additives to a certain fluoropolymer to prevent bubbling of the rotolining, the rejection asserts that since some of these additives are the same as those of Applicant's claims, then the Kazumi additives will also promote adhesion. The certain fluoropolymer used in Kazumi is called PFA. Claims 6, 12, 14, and 19-21 are all novel over Kazumi by reciting that the TFE/PAVE copolymer is stabilized by fluorine treatment. Kazumi does not disclose such stabilizing treatment for its PFA. Moreover, it is apparent that the Kazumi PFA is not stabilized by the fact that it bubbles during rotolining, which is why the inorganic powder or metal powder is added to the PFA. Fluorine-stabilized TFE/PAVE does not bubble during rotolining (p. 3, l. 11-29).

As is well known in the art, TFE/PAVE or PFA does not adhere to the molding surface in rotolining (p. 1, l. 30-39). Rather than assume that Kazumi obtains adhesion, one skilled in the art would understand Kazumi's silence on adhesion as not obtaining adhesion. Certainly, Kazumi does not suggest that its teaching is the place to look for solving the non-adhesion problem.

The assertion that Kazumi will obtain adhesion is an assertion of inherency. Applicant's Examples disclose that adhesion to obtain the minimum peel strength of 25 lb/in occurs only at very small amounts of metal powder content. The Copolymer A disclosed in the Table in Example 5 losses considerable peel strength when the Zn content increases from 0.5 wt% to 1.0 wt%. When the Zn content is increased to 3 wt% in Example 6, the peel strength reduces to about one-half of that obtained when the Zn content is 1.0 wt%, to less than 25 lb/in. The mere disclosure of the 0.1 to 30% additive fine powder range and the preferred 5% amount [0018] applied to the fine powders 6 mentioned, i.e. inorganic powder or metal powder such as glass, silicon, zinc, aluminum and copper [0016] does not necessarily inherently obtain any adhesion result, much less the minimum of 25 lb/in recited in claim 6 (and claim 25). The fact that a certain effect may result from a given set of circumstances is not sufficient to establish inherency, In re Oelrich, 212 USPQ 323, 326 (CCPA 1981). The extreme variability in results within the Kazumi disclosure of additive range and additive choice is illustrated by the fact that use of aluminum metal powder at the 0.5 and 1.0 wt% loading in the TFE/PAVE produces bubbles (p. 16, l. 6-10).

The English translation of Kazumi supplied with the IDS is a machine translation. Section [0016] referred to above is garbled. A translator translation has therefore been obtained and is attached hereto to provide a more understandable reading of section [0016].

Should it be of interest, an assertion of inherency does not form a proper basis for an allegation of obviousness. As stated in In re Spormann and Heinke, 150 USPQ 449, 452 ((CCPA 1966):

> "As we pointed out in In re Adams, 53 CCPA 996, 356 F2d 998, 148 USPQ 742, the inherency of an advantage and its obviousness are entirely different questions. That which may be inherent is not necessarily known. Obviousness cannot be predicated on what is unknown". (p. 452)

Adhesion is unknown from Kazumi. The problem solved by the present invention is how to adhere a TFE/PAVE lining that is bubble-free by itself to the mold surface. Kazumi's silence on adhesion gives no hint on how to solve the problem. Indeed, it can only be knowledge of the present invention, not the prior art that guides the reliance on Kazumi for rejecting Applicant's claims.

Claims 24 and 25 directed to MFA copolymer is novel over Kazumi in that it is apparent that the PFA copolymer referred to in Kazumi is not MFA, which is a copolymer of TFE/PMVE/PPVE (p. 7, l. 13-20). That this is consistent with Kazumi's intention and therefore would be so-understood by one skilled in the art from Kazumi is indicated by Chapter 21 of J. Scheirs, Modern Fluoropolymers, High Performance Polymers for Diverse Applications, published by John Wiley & Sons (1997), pp. 373-376 attached hereto. MFA is distinguished from PFA in the first full paragraph on p. 374 and the separate reference to PFA and MFA is disclosed on p. 375, 4th and 5th paragraphs and in Table 21.1 on p. 376. U.S. Patent 6,642,269 (copy attached), referred to in an IDS, discloses the formation of bubble free rotomoldings from MFA by itself (see col. 10, l. 56-57 and col. 11, l. 26-27). The present invention, not Kazumi, has discovered how to adhere the bubble-free MFA rotomolding to the mold surface so as to become a rotolining.

Claims 12, 14, and 19 are novel and patentable over Kazumi on the same basis as claim 6.

Claims 20 and 21 are also novel and patentable over Kazumi on the basis of reciting the combination of stable TFE/PAVE and the small amount of metal powder enabling an adhesion result not disclosed, suggested or being necessarily inherently present in Kazumi. New claims 22-23 are patentable on the same basis as claim 20. In addition, the 0.3 to 1.2 wt% range for the metal powder and its adhesion effect is not disclosed or suggested by Kazumi. The subject matter of claim 23 recites a mixture which is considered unsuitable in Saito (paragraph bridging cols. 4 and 5), cited against claims 1-2, 4-5, 8-9, and 13 for the

disclosure of creating a bubble-free layer of PFA and rotolining thickness of up to 5 mm. The PFA lining in Saito achieves its bubble-free PFA coating thickness results by virtue of its teaching in totality, which includes the requirement that the combination of additives to the PFA must be present in the PFA granules. Claim 23 derives patentability by being directed at the Saito-unsuitable subject matter and yet achieving a good result.

New claims 26 and 27 are novel and patentable on the same basis as discussed with respect to claims 6, 22, and 23 above.

New claim 28 is directed to a very thick overcoat (at least 4 mm) as compared to the 0.5 to 1 mm second layer thickness in Kazumi [0021] selected so as to avoid the formation of bubbles in the second layer [0022]. The disclosure of lining thickness up to 5 mm in Saito (col. 1, l. 58-61) gives no hint how this greater thickness would be applicable to the overcome the bubble limitation on the second layer thickness disclosed in Kazumi. Saito does not suggest how to increase the Kazumi second layer thickness without forming bubbles. The Saito topcoat is only 1 mm thick (col. 12, l. 20-25), which is only one-half the thickness of the 2 mm thick lining (undercoat)(col. 11, l. 9). The teachings of Saito and Kazumi, taken individually or collectively simply fail to suggest the much greater overcoat thickness of claim 28..

With respect to the obviousness rejection of claims 15 and 16 based on Kazumi, these claims are patentable over Kazumi on the same basis as parent claim 6.

With respect to the obviousness rejection (Kazumi in view of Saito) of claims 1-2, 4-5, 8-9, and 13, now applicable to claims 2, 5, 8-9 and 13, these claims all depend ultimately on claim 6 and are patentable over Kazumi on the same basis as discussed above with respect to claim 6. In addition, the overcoat having the thicknesses recited in claims 2, 4, 8, and 9 are all patentably distinguishable from the limited second layer thickness of 0.5 to 1.0 mm disclosed in Kazumi. Saito does not solve the bubble problem for the second layer in Kazumi so as to obtain the relationships recited in these claims. With respect to claim 13, the disclosure of tin in Saito is with respect to the disadvantage of using heat stabilizers to prevent PFA powder coating from bubbling. One skilled in the art would see no recommendation from this negative disclosure to use tin in Kazumi. Most important is the fact that tin thermal stabilizer disclosed in Saito is irrelevant to the claimed invention using fluorine treatment stabilized TFE/PAVE, which therefore does not require any added stabilizer to prevent bubble formation.

Buckmaster is added to Kazumi and Saito for the obviousness rejection of claim 3, which is now cancelled. Claims 6 and 20 are now directed to this subject matter, including the further requirement that this stabilization is obtained by fluorine treatment, which is considered undesirable in Buckmaster (col. 2, l. 3-11), to be replaced by the different Buckmaster stabilizing treatment with secondary or tertiary amine in order to obtain $-CF_2H$ end groups (col. 3, l. 3-12). The fluorine treatment provides the stable –CF3 end group (p. 3,

l. 20). The rejection refers to the knowledge in the art to remove unstable end groups as being the basis for importing Buckmaster into Kazumi/Saito. This approach overlooks the fact that the present invention is not working to improve Kazumi. The starting point of the invention of claims 6 and 20 is TFE/PAVE that has no bubble problem and therefore needs no additive from Kazumi for any purpose. Kazumi's silence on adhesion gives no hint of Applicant's solution to the problem, but does indicate that the rejection is based on impermissible hindsight. As discussed above with respect to claim 6, the assertion of inherency is untenable both factually and legally as a basis for the obviousness rejection.

With respect to the obviousness ejection of claims 17 and 18 based on Kazumi in view of Buckmaster, these claims are patentable on the same basis as the parent claim 6.

A petition of one-month extension of time and payment of the required fee and payment for one additional independent claim is filed herewith.

In view of the foregoing, allowance of the above-referenced application is respectfully requested.

Respectfully submitted,

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(54) FLUORORESIN LINING CHEMICAL CONTAINER AND METHOD OF MANUFACTURE THEREOF

CLAIMS

1. A fluororesin lining chemical container, characterized by the fact that in a chemical container in which a lining layer is formed on the inner surface of said container by rotating and spreading a heat-fusible fluororesin in a container body made of metal, the above-mentioned lining layer consists of at least a first resin layer in which a fine powder is mixed; and a second resin layer that is formed on the upper layer of the first resin layer and suppresses the precipitation of the above-mentioned fine powder material.

2. The fluororesin lining chemical container of Claim 1, characterized by the fact that the first and second lining layers composed of the above-mentioned heat-fusible fluororesin are composed of a copolymer of ethylene tetrafluoride and perfluoroalkoxyethylene.

3. The fluororesin lining chemical container of Claim 1 or Claim 2, characterized by the fact that a container body made of metal, an opening tube formed of a synthetic resin installed at an opening part of said container body, an injection and discharge tube that is fitted to said opening tube and connects the space in the container body to the outside, and a cap spirally fixed to the above-mentioned opening tube to prevent the separation of said injection and discharge tube are provided; the lining layer consisting of the first resin layer in which a fine powder is mixed to prevent bubble generation during lining and the second resin layer that is formed on the upper layer of the first resin layer and suppresses the precipitation of the above-mentioned fine powder are formed on the inner surface of the above-mentioned container body; the above-mentioned opening tube is provided with an O-ring mounting surface formed stepwise at its inner wall; the outer periphery of the above-mentioned injection and discharge tube is provided with an O-ring pressure surface corresponding to the above-mentioned O-ring mounting surface; and an O-ring loaded between the above-mentioned O-ring mounting surface and O-ring pressure surface is elastically deformed in the horizontal direction of the opening part by the pressure of the above-mentioned injection and discharge tube against the opening tube, and airtightly closes the contact part of the above-mentioned injection and discharge tube and the opening tube.

4. A method for manufacturing a fluororesin lining chemical container, characterized by the fact that a first lining layer is formed on the inner surface of the container body by injecting a first heat-fusible fluororesin mixed with a fine powder into a container body made of metal, and rotating the container body while heating; and a second lining layer is formed on the upper layer of the above-mentioned first lining layer of the inner surface of the container body by injecting a second heat-fusible fluororesin into the above-mentioned container body, and rotating the container body while heating.

DETAILED EXPLANATION OF THE INVENTION

[0001]

Industrial application field

The present invention pertains to a container made of metal with chemical resistance and its manufacturing method.

[0002]

Prior art

As such a container made of metal, in order to render a chemical resistance to it, an interior bag of a synthetic resin is inserted into the container body, or a resin is lined on the inner surface of the container body by an electrostatic coating, or a sheet composed of a synthetic resin is adhered to the inner surface of the container body by a plastic welding.

[0003]

However, in case the interior bag was used, the possibility of said interior bag not being adhered to the inner surface of the container body and chemicals penetrating into the container made of metal was high.

[0004]

Also, the electrostatic coating had a layer thickness of 0.5 mm or smaller, and the corrosion resistance was not sufficient. Furthermore, in the sheet lining, there was a possibility that impurities were mixed into the welded part, degrading the chemical resistance of the part.

[0005]

In consideration of the above-mentioned problems, the present invention proposes a technique that injects a heat-fusible fluororesin into a container body while rotating said container body made of metal in a heating state and applies the lining that is proposed in Japanese Patent Application No. Hei 2[1990]-338899.

[0006]

Problems to be solved by the invention

On the other hand, during the above-mentioned rotating and lining, the heat-fusible fluororesin generates bubbles, and a bubble space is sometimes scattered into the resin layer being generated. The presence of bubble space in the resin layer lowers the corrosion resistance of this part, degrading the container performances.

[0007]

Accordingly, an inorganic powder or metal powder such as glass, silicon, zinc, aluminum (Al), copper (Cu), etc., is mixed into the above-mentioned fluororesin to suppress bubble generation.

[0008]

On the other hand, this inventor newly discovered that in this chemical container, if the resin layer was formed by mixing the above-mentioned fine powder into the resin, a fine powder mixed in the vicinity of the layer surface was precipitated, altering the characteristic of the chemicals being housed, or chemically changing the fine powder itself by the chemicals, so that there was a possibility that the corrosion resistance was degraded.

[0009]

The purpose of the present invention is to provide a technique that can obtain a chemical container with high chemical resistance by suppressing the precipitation of a fine powder material to the surface of a resin layer while preventing bubble generation in the resin layer.

[0010]

Means to solve the problems

The essence of the present invention is a fluororesin lining chemical container characterized by the fact that in a chemical container in which a lining layer is formed on the inner surface of said container by rotating and spreading a heat-fusible fluororesin in a container body made of metal, the above-mentioned lining layer consists of at least a first resin layer in which a fine powder is mixed; and a second resin layer that is formed on the upper layer of the first resin layer and suppresses the precipitation of the above-mentioned fine powder material.

[0011]

Operation

According to the above-mentioned means, in forming the first resin layer, a fine powder is mixed into the resin, so that bubbles in the resin are discharged to the outside by a free movement of the fine powder in the molten resin, preventing the bubbles from remaining in the resin.

[0012]

Also, by forming the second resin layer on the upper layer of the first resin layer mixed with the above-mentioned fine powder, the precipitation of the above-mentioned fine powder material can be suppressed.

[0013]

Application example

The chemical container of the present invention has a container body 1 with an inner volume of 100 L made of stainless steel, and in an opening part 2 of the container body 1, an opening tube 10 formed of an ethylene tetrafluoride resin (PTFE) is inserted in a body with the above-mentioned container body 1. On the upper surface of the above-mentioned opening tube 10, a contact surface 13 is formed, and a collar 5 of an injection and discharge tube 20, which will be mentioned later, contacts with the contact surface 13. Then, an O-ring mounting surface 11 is formed stepwise on the inner peripheral surface of said opening tube 10 (a side wall 12 of the opening tube), and an O-ring 30 formed of an elastic material such as synthetic rubber is mounted on the O-ring mounting surface 11.

[0014]

Then, a lining layer 3 with a double layer structure is formed on the inner surface of the above-mentioned container body 1.

[0015]

Next, the method for manufacturing and assembling the above-mentioned chemical container is explained according to the sequence. First, the container body is mounted on a pair of support rollers not shown in the figure, and said container body 1 is rotated around the axis of the container body 1 while heating it to about 370-410°C.

[0016]

Then, during the rotation, a copolymer (PFA) of ethylene tetrafluoride and perfluoroalkoxyethylene as a heat-fusible fluororesin is injected from the above-mentioned opening part 2 in an open state. In the PFA, a fine powder 6 composed of an inorganic powder or metal powder such as glass, silicon, zinc, aluminum (Al), and copper (Cu) is mixed.

[0017]

In the lining of the above-mentioned resin, bubbles are generated in the PFA in a molten state, however said bubbles are attached to the fine powder 6 being freely moved in the PFA and discharged to the outside. This way, no bubbles remain in the PFA.

[0018]

As the amount of said fine powder 6 being mixed, the fine powder can be mixed in a range of about 0.1-30% into the PFA, and the amount of fine powder being mixed in a range of about 5% is most effective for removing the bubbles.

[0019]

Next, the above-mentioned PFA is cured by cooling the container body 1, so that a first resin layer 3a with a layer thickness of 2 mm is obtained on the inner surface of the container body 1.

[0020]

Next, while heating up to 370-410°C by rotating the container body 1, similarly to the above-mentioned case, the PFA is injected into the container body 1. In the PFA injected at the second time, the fine powder 6 used in the above-mentioned first PFA injection is not mixed. Also, the amount may be small compared to the above-mentioned first PFA.

[0021]

In the second resin lining, a second resin layer 3b with a layer thickness of 0.5-1.0 mm is obtained on the surface of the above-mentioned first resin layer 3a.

[0022]

Since the thickness of the above-mentioned second resin layer 3b is smaller than that of the above-mentioned first resin layer 3a, the bubble generation themselves is very little. Therefore, in the formation of the second resin layer 3b, it is not necessary to mix the fine powder 6 into the PFA.

[0023]

Furthermore, the reason why the layer thickness is set to 0.5-1.0 mm is that the layer thickness in this range is necessary and sufficient to suppress the precipitation of the fine powder material from the above-mentioned first resin layer 3a.

[0024]

In the container body 1 in which the lining layer 3 consisting of the first and second resin layers 3a and 3b has been formed on the inner surface, a resin coat 4 composed of a polyethylene resin with a thickness of 0.2 mm is further formed on its outer surface.

[0025]

In the formation of the resin coat 4, a support not shown in the figure is inserted into the container body 1, and while rotating the support, the above-mentioned polyethylene resin is coated.

[0026]

Then, the above-mentioned coating thickness is required to be at least 0.1 mm or greater, and as its material, polypropylene (PP), polyvinyl chloride (PVC), etc., can be used in addition to the above-mentioned polyethylene (PE).

[0027]

Next, the injection and discharge tube 20 is inserted into the opening tube 10 of the container body 1. On the outer peripheral surface of the injection and discharge tube 20, a stepped O-ring pressure surface 21 is provided at the position corresponding to the O-ring mounting surface 11 of the above-mentioned opening tube 10, and the O-ring 30 is elastically formed in the direction of side wall 12 of an opening tube and side wall 22 of an injection and discharge tube by the force from the above-mentioned O-ring mounting surface 11 and O-ring pressure surface 21 through the pressure of the above-mentioned injection and discharge tube 20 and forces of both side walls.

[0028]

Thus, since the O-ring 30 is forced and closely adhered to four surfaces of the O-ring mounting surface 11, O-ring pressure surface 21, side wall 12 of the opening tube, and side wall 22 of the injection and discharge tube, the opening tube 10 and the injection and discharge tube 20 are sealed and closed, so that the leak of an internal chemical liquid is completely prevented.

[0029]

Also, a fixed pressure or more of the above-mentioned injection and discharge tube 20 against the opening tube 10 is suppressed since the collar 5 of the injection and discharge tube 20 contacts with the contact surface 13. Thus, the collapse due to the excessive pressure of the O-ring 30 can be prevented.

[0030]

In general, the O-ring 30 has a possibility to collapse that is caused by the pressure more than is necessary and that the sealability is degraded, however in this application example, since

the pressure of the injection tube 20 more than is necessary is suppressed by the contact surface 13 as mentioned above, there is no such a concern.

[0031]

Then, finally, a cap 35 is spirally fixed to the above-mentioned opening tube 10, so that the separation of the injection and discharge tube 20 is prevented.

[0032]

As mentioned above, according to this application example, the lining layer 3 has a laminated structure, and in forming the first resin layer 3a, the generation of bubble is suppressed by mixing the fine powder 6 into the resin. Also, with the formation of the second resin layer 3b on the upper layer of the first resin layer 3a, the precipitation of the above-mentioned fine powder material is suppressed.

[0033]

Furthermore, in pressing the injection and discharge tube 20 against the opening part 2, since the O-ring 30 is forced in four surface directions and the pressure more than is necessary is suppressed, a sealing inferiority due to an insufficient pressure or a sealing inferiority due to the collapse of the O-ring resulting from an excessive pressure can be prevented, providing a chemical container with high sealing reliability.

[0034]

Effects of the invention

According to the present invention, the lining layer 3 has a laminated structure of the first resin layer mixed with the fine powder 6, and the second resin layer for suppressing the precipitation of the fine powder material, providing a chemical container with high chemical resistance.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a cross section showing an outlined structure of the chemical container as an application example of the present invention.

Figure 2 is a cross section showing the vicinity of an opening part of the chemical container in the application example.

Figure 3 is a partial cross section showing part of the chemical container in the application example.

Explanation of symbols:

1	Container body
2	Opening part
3	Lining layer
3a	Resin layer
3b	Resin layer
4	Resin coated film
5	Collar
6	Fine powder
10	Opening tube
11	O-ring mounting surface
12	Side wall of an opening tube
13	Contact surface
20	Injection and discharge tube
21	O-ring pressure surface
22	Side wall of an injection and discharge tube
30	O-ring
35	Cap

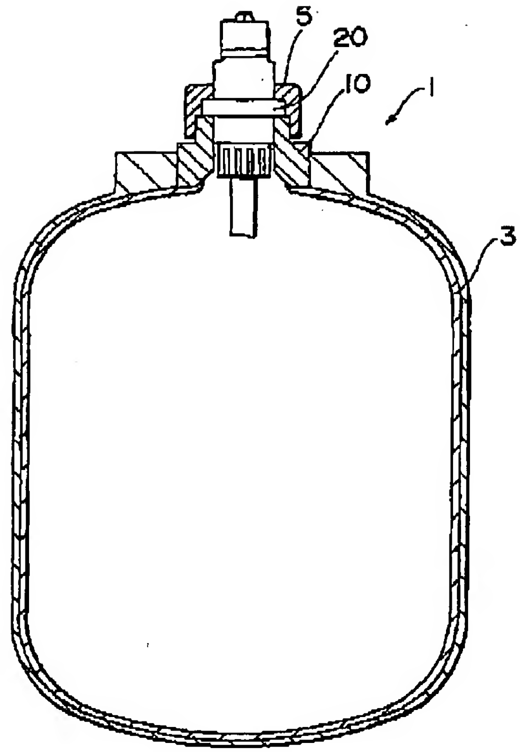

Figure 1

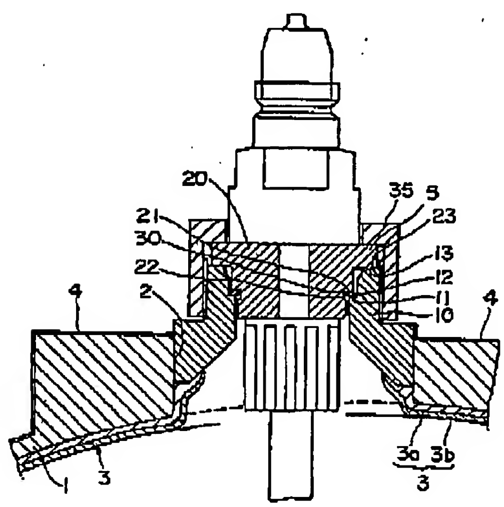

Figure 2

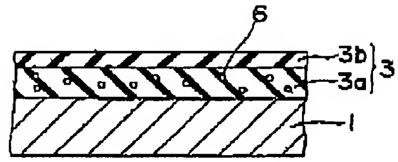

Figure 3

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Modern Fluoropolymers

High Performance Polymers for Diverse Applications

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21

Melt-processable Perfluoropolymers

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1 INTRODUCTION

The development of fluorine-containing polymers followed the synthesis of low molecular weight polychlorotrifluoroethylene (PCTFE) [1] and the accidental discovery of polytetrafluoroethylene (PTFE) [2] in the late 1930s.

The unique combination of properties of PTFE was immediately apparent, like the difficulties of transforming it into appropriate shapes. In fact the melt viscosity of PTFE is in excess of 10 billion poise, and transformation techniques similar to metal sintering and ceramics have to be used, such as sintering of granular resin from suspension polymerization grades and past extrusion of fine powders from emulsion polymerization grades.

The need for easier processable resins led to the development of different highly fluorinated plastics. Although many fluoropolymers have been prepared, since the discovery of PTFE, major commercial products are homopolymers and copolymers deriving from free radical polymerization of a limited number of fluoromonomers, such as tetrafluoroethylene (TFE), vinyl fluoride (VF), vinylidene fluoride (VF_2), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), perfluoropropylvinylether (PVE) and more recently perfluoromethylvinylether (MVE).

Melt-processable perfluoropolymers, detailed in the present chapter, derive from the need for having a resin with PTFE properties but able to be transformed by conventional melt-processing techniques.

The copolymer of TFE and HFP [3], known as fluorinated ethylene propylene (FEP) copolymer, was the first melt-processable perfluoropolymer, having a melt

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viscosity low enough for conventional melt processing. However, FEP does not have the same heat stability and high-temperature properties as does the homopolymer of TFE, so copolymers of TFE and PVE, known as perfluoroalkoxy polymers (PFA) [4] have been developed. These polymers possess a thermal stability closer to that of PTFE, and can be used at the same continuous service temperature (260 °C).

The cost of PFA is higher than FEP due to the higher cost of the PVE monomer compared to HFP. Economically attractive perfluorovinylethers–TFE copolymers have been recently introduced on the market, due to the use of different technologies for both monomer preparation and polymerization [5,6]. These new perfluoropolymers are obtained by copolymerizing TFE with the MVE monomer, and named MFA to distinguish them from the conventional PFA's.

2 CHEMICAL STRUCTURE AND RELATED PROPERTIES

Highly fluorinated plastics have gained a great commercial importance thanks to a unique combination of high thermal stability, outstanding resistance to most chemicals, low surface energy, low dielectric constant and dissipation factor, excellent weatherability, low moisture adsorption and low flammability.

The above properties are maximized in the case of perfluoropolymers, although partially fluorinated plastics possess some their own unique properties.

Since the late 1930s, following the discovery of polytetrafluoroethylene (PTFE), it was recognized that a fluorinated macromolecular chain possesses unique properties of thermal stability and chemical inertness [7].

In PTFE these two characteristics appear to be maximized. In fact it possesses a very high melt viscosity at high temperature (10^{12} poises at 360 °C), a high crystalline melting point (327 °C) and a high thermal stability. It is notable that this polymer, if we consider the other extreme of the temperature spectrum, also possesses unusual toughness at a temperature as low as 4 K.

Furthermore perfluorocarbon polymers are practically insoluble in all common solvents and highly resistant to any chemical attack. These unusual properties can be attributed to:

- high bond energy of C–F and C–C link
- low secondary bonding forces
- relatively small size of fluorine

Bond energy of C–F and C–C in fluorocarbons is higher than that of C–H and C–C in hydrocarbons. The C–F bond energy goes from 447 kJ/mol for the CH_3F to 485 kJ/mol for the CF_4 and remains much higher than that of the C–H link [8,9]. The C–C bond energy rises from an average value of 348 kJ/mol for hydrocarbon systems to 360 kJ/mol in fluorocarbons [9,10]. The high bond energies of C–F and to a lesser extent of C–C links mostly account for the high

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thermal stability of fluorocarbons and their high resistance to radical assisted abstraction of F from a C–F bond. Van der Waals' forces for simple hydrocarbons and fluorocarbons are reported to be about 40 and 4 kJ/mol respectively, that is, fluorine-based materials show second bonding forces about 10 times lower than corresponding hydrocarbons [11].

An interesting consequence of this property is the similarity between boiling points of fluorocarbons and homologues hydrocarbons [11]. As the molecular weight of fluorocarbons is considerably higher than hydrocarbons at constant carbon number, a higher boiling point should be expected. In fluorocarbons the decreased van der Waals' attractive forces offset the increased molecular weight. Intermolecular forces in PTFE are only 3.18 kJ/mol, at least in part attributed to the crowding of fluorine atoms which protect and isolate the carbon backbone reducing the interaction between different macromolecular chains. Covalent radii of fluorine and hydrogen are respectively 0.72 Å and 0.37 Å. The increase of the number of fluorine atoms attached to the same carbon atom reduces the C–F bond length, which is accompanied by an increase in bond energy. The large size of fluorine accompanied by the C–F bond shortening can have important consequences in highly fluorinated fluorocarbon polymers. Probably the most important is the increased resistance to chemical attack which arises from the shielding action of fluorine on the carbon backbone and C–F bond strength. A further important consequence of the high bond energy of the C–F link, one of the strongest in organic compounds, is related to the polymerization chemistry of fluorinated monomers and subsequent derivable structures.

The high C–F bond energy prevents chain transfer reaction to polymer through the C–F group during the polymerization reaction, since this reaction is very unlikely on the basis of kinetic and thermodynamic factors under the usual polymerization conditions [12]. This means that generally perfluorocarbon polymers should be less branched than homologous hydrogenated polymers and the increase of the fluorine content in the fluoropolymer should reduce the degree of branching.

The most important evidence of the linear structure of perfluorocarbon polymers is demonstrated by PTFE, which has a degree of crystallinity as high as 93–98%. Such a high level of crystallinity can be obtained only with substantially unbranched structures [12].

The introduction of bulky groups, such as HFP, PVE or MVE, in the PTFE structure, to obtain FEP, PFA and MFA polymers, reduces the crystalline order and reduces the crystallization of the macromolecular chains. The size of the bulky group determines the amount of comonomer needed to obtain the desired degree of structural disorder. The larger the size of the bulky group, the lower is the amount of comonomer needed, and the correspondingly higher melting point that is obtained as shown in Table 21.1.

The higher stability of PFA and MFA polymers compared to HFP can be attributed to the less steric bond strain of the vinylether monomers used. Because, in this case, the bulky group is attacked to backbone by an ether link [13].

Table 21.1. Main comonomers used in TFE-based perfluoropolymers

Perfluoropolymer	Comonomer	Mol %	T(°C)
FEP	$CF_2=CF-CF_3$	5–6	265
MFA	$CF_2=CF-O-CF_3$	3–4	285
PFA	$CF_2=CF-O-CF_2-CF_2-CF_3$	1–2	305

3 MONOMER PREPARATION

3.1 *TETRAFLUOROETHYLENE (TFE)–HEXAFLUOROPROPYLENE (HFP)*

The preparation of the basic fluoromonomers, TFE and HFP, can be achieved by the hydrofluorination of chloroform to give chlorodifluoromethane (CFC22) as follows: [14,15]

$$CHCl_3 + 2HF \longrightarrow CHClF_2 + 2HCl$$

The reaction proceeds at temperatures between 80 and 100 °C and a catalyst should be present such as antimony chlorofluoride. The CFC22 is pyrolyzed at high temperature and gives TFE plus by-products. In a silver tubular reactor heated by an electric furnace a selectivity of 93% for TFE and 1% for HFP with 38.4% CFC22 conversion was obtained at a temperature of 687 °C and a contact time of 1.8 seconds [16]. The reaction mechanism of the CFC22 pyrolysis is supposed to pass from an unstable intermediate, i.e. difluorocarbene, which subsequently forms TFE. The reaction scheme can be as follows:

$$CHClF_2 \xrightarrow{\text{heat}} (CF_2) + HCl$$

$$2(CF_2) \xrightarrow{\text{heat}} CF_2{=}CF_2 + SP(\text{byproducts})$$